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RATE CONSTANTS  
FOR CALCULATIONS ON  
NOZZLE AND ROCKET EXHAUST  
FLOW FIELDS

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SUMMARY

A list of rate constants of reactions important in nozzle and rocket exhaust flow fields is given. Rate constants (expressed as functions of temperature) are either taken directly from the best experiments described in the literature or estimated by comparison with known rate constants for similar reactions and with theory. Estimates of probable errors in rate constants are included, and give the engineer likely to use the rate constants a feeling for the uncertainties in these numbers.

### ACKNOWLEDGEMENTS

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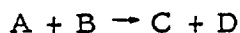
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## I. INTRODUCTION

This report contains a list of rate constants compiled at AeroChem for use in calculations on chemical composition, pressure, and temperature in nozzles and afterburning exhaust plumes. Spatial distributions of composition, temperature, and pressure calculated via computer programs which take account of departures from chemical equilibrium can be quite different from those obtained when full chemical equilibrium is assumed to be established throughout an exhaust or when frozen flow calculations are made,<sup>1</sup> and the practical need for information concerning rates of reactions of species present in nozzles and exhaust plumes is thus clear. The reactions whose rate constants are listed in no sense constitute a reaction mechanism for any particular system; the reactions to be incorporated in the reaction scheme for any given calculation must be selected in the light of the particular characteristics (e.g., propellant composition) of the system under consideration.

The authors offer the following important observations to the reader:

(1) The "rate constants" listed are defined in the manner usually adopted in descriptions of chemical rate processes. Thus, for example, the rate constant  $k$  of the reaction



is defined by

$$-\frac{dn_A}{dt} = k n_A n_B$$

All rate constants are expressed in molecule-cm-sec units, which the authors feel to be the logical units for gas-phase reactions; centimeters are used more widely by chemists than meters, and reaction rate theories describe rates in terms of collisions between molecules rather than moles. All temperatures are expressed in  $^{\circ}\text{K}$  and all activation energies in cal/mole.

(2) The rate constants given are based, as far as possible, on experimental measurements. Where no measurements are available (this applies to a large number of reactions), rate constants are estimated by comparison with those for similar reactions, allowance being made in the light of collisional and transition state theories for probable steric, reduced-mass, and cross-section differences. It would seem difficult to justify a more rigorous approach

to the estimation of undetermined rate constants at present: despite encouraging recent progress on theoretical calculations, these calculations are not yet generally reliable. We would suggest that under no circumstances should any reader make use of a rate constant without considering the comment indicating the source of our value.

(3) The rate constants given are intended for use in calculations for systems at temperatures between 1000 and 3500<sup>0</sup>K. All kineticists will appreciate the fact that our expressions of temperature dependences are greatly oversimplified by theoretical standards; in almost all cases, however, the experimental data do not warrant use of more complicated expressions.

(4) The upper possible error factor is defined as the ratio of our estimate of the probable upper limit of the rate constant to our estimated rate constant  $k$  itself at the temperature at which the rate constant is least accurately known. The lower possible error factor is the ratio of  $k$  to our estimate of the probable lower limiting value of the rate constant at this temperature. These error factors are the result of reasonable semi-quantitative appraisal rather than detailed statistical analysis of the available data and are intended principally to give the engineer a feeling for the uncertainty in each rate constant. The factors are usually considerably larger than the uncertainties attached to their results by the original experimentors; this is almost always because we have had to extrapolate available results into temperature ranges considerably different from those of the experiments themselves.

(5) Two difficulties arise in the case of reactions involving third bodies (e.g., reactions in Groups A, E, F, and G). The first is that different third bodies have different (and often unknown) efficiencies in these reactions; we have tried to give rate constants averaged for the more effective third bodies (usually H<sub>2</sub>O, CO<sub>2</sub>, N<sub>2</sub>, HCl, etc.) in a typical exhaust. The deficiencies of this averaging process are obvious; our defense of its use is simply that the errors which it introduces are generally small by comparison with possible errors in the rate constants for individual third bodies. A second difficulty is that the third body reactions (and their reverse reactions) actually take place via stepwise processes involving excited molecular or atomic states, and one should really take account of individual reactions of these states rather than choose, as we have done, overall rate constants for overall artificial reactions. This is unfortunately impossible to do at present. Other formal descriptions of the chemical kinetic processes occurring in a system (e.g., those in terms of cross sections expressed as functions of molecular energy rather than in terms of rate constants expressed as functions of temperature), which in the future will probably result in solution of this problem, lead at present to even greater problems. In connection with this difficulty, we should point out that "collision

frequencies" referred to in the notes on reactions are really collision frequencies calculated on the assumption that all molecules are in ground electronic, vibrational and rotational states. This misleading terminology is in common use.

(6) The values of rate constants given are considered to be the best which can be gleaned from the literature published up to December 1966.

(7) The method of numbering reactions is that found convenient in practice at AeroChem (where values for rate constants are frequently updated); it enables us to keep arbitrarily related reactions in groups.

(8) The rate quotient law (which states that the ratio of the rate constant for a forward reaction to that of the reverse reaction is equal to the equilibrium constant) is assumed to hold for all the reactions considered. Recent theoretical and experimental evidence of apparent deviations from this law (which are the consequences of incorrect descriptions of reactions - see Ref. 65) have not yet crystallized sufficiently for us to take any other view.

(9) The notes on rate constants are very brief; to acknowledge all the valuable kinetic work not mentioned would greatly increase the length of the report and the time required for its preparation.

II. LIST OF RATE CONSTANTS

No.	Reaction	Rate Constant, k, cm-molecule-sec units	Possible Error Factor	
			Upper	Lower
A1	$O+O+M \rightarrow O_2 + M$	$1 \times 10^{-29} T^{-1}$	10	10
A2	$O+H+M \rightarrow OH+M$	$1 \times 10^{-29} T^{-1}$	10	10
A3	$H+H+M \rightarrow H_2+M$	$1 \times 10^{-29} T^{-1}$	5	5
A4	$H+OH+M \rightarrow H_2O+M$	$1 \times 10^{-28} T^{-1}$	10	10
A5	$CO+O+M \rightarrow CO_2+M$	$5 \times 10^{-29} T^{-1} e^{-4000/RT}$	3	30
A6	$OH+OH \rightarrow H_2O+O$	$1 \times 10^{-11} e^{-1000/RT}$	5	5
B1	$OH+H_2 \rightarrow H_2O+H$	$4 \times 10^{-11} e^{-5500/RT}$	3	3
B2	$O+H_2 \rightarrow OH+H$	$3 \times 10^{-11} e^{-8200/RT}$	5	5
B3	$H+O_2 \rightarrow OH+O$	$3 \times 10^{-10} e^{-16500/RT}$	1.5	1.5
B4	$CO+OH \rightarrow CO_2+H$	$5 \times 10^{-13} e^{-600/RT}$	5	5
C1	$H+Cl_2 \rightarrow HCl+Cl$	$7 \times 10^{-10} e^{-3000/RT}$	5	5
C2	$Cl+H_2 \rightarrow HCl+H$	$1.5 \times 10^{-10} e^{-5600/RT}$	5	5
C3	$H_2O+Cl \rightarrow HCl+OH$	$5 \times 10^{-11} e^{-19000/RT}$	30	30
C4	$OH+Cl \rightarrow HCl+O$	$3 \times 10^{-11} e^{-5000/RT}$	30	30
C5	$H+HF \rightarrow H_2+F$	$2 \times 10^{-11} e^{-35000/RT}$	5	5
C6	$H+F_2 \rightarrow HF+F$	$7 \times 10^{-10} e^{-3000/RT}$	10	10
D1	$Li+HCl \rightarrow LiCl+H$	$3 \times 10^{-10}$	10	30
D2	$Na+HCl \rightarrow NaCl+H$	$3 \times 10^{-10} e^{-5000/RT}$	10	30
D3	$K+HCl \rightarrow KCl+H$	$3 \times 10^{-10}$	10	30
D4	$Cs+HCl \rightarrow CsCl+H$	$3 \times 10^{-10}$	10	30
D5	$Li+H_2O \rightarrow LiOH+H$	$3 \times 10^{-11} e^{-20000/RT}$	30	30
D6	$Na+H_2O \rightarrow NaOH+H$	$3 \times 10^{-11} e^{-44000/RT}$	30	30
D7	$K+H_2O \rightarrow KOH+H$	$3 \times 10^{-11} e^{-40000/RT}$	30	30
D8	$Cs+H_2O \rightarrow CsOH+H$	$3 \times 10^{-11} e^{-31000/RT}$	30	30
E1	$H+Cl+M \rightarrow HCl+M$	$3 \times 10^{-29} T^{-1}$	10	30



II. LIST OF RATE CONSTANTS cont'd

No.	Reaction	Rate Constant, k, cm-molecule-sec units	Possible Error Factor	
			Upper	Lower
E2	$\text{Cl} + \text{Cl} + \text{M} \rightarrow \text{Cl}_2 + \text{M}$	$3 \times 10^{-29} \text{T}^{-1}$	10	10
E3	$\text{H} + \text{F} + \text{M} \rightarrow \text{HF} + \text{M}$	$1 \times 10^{-28} \text{T}^{-1}$	10	10
E4	$\text{F} + \text{F} + \text{M} \rightarrow \text{F}_2 + \text{M}$	$3 \times 10^{-30} \text{T}^{-1.5}$	10	10
F1	$\text{Li} + \text{OH} + \text{M} \rightarrow \text{LiOH} + \text{M}$	$3 \times 10^{-28} \text{T}^{-1}$	10	30
F2	$\text{Na} + \text{OH} + \text{M} \rightarrow \text{NaOH} + \text{M}$	$3 \times 10^{-28} \text{T}^{-1}$	10	30
F3	$\text{K} + \text{OH} + \text{M} \rightarrow \text{KOH} + \text{M}$	$3 \times 10^{-28} \text{T}^{-1}$	10	30
F4	$\text{Cs} + \text{OH} + \text{M} \rightarrow \text{CsOH} + \text{M}$	$3 \times 10^{-28} \text{T}^{-1}$	10	30
F5	$\text{Li} + \text{Cl} + \text{M} \rightarrow \text{LiCl} + \text{M}$	$1 \times 10^{-28} \text{T}^{-1}$	30	100
F6	$\text{Na} + \text{Cl} + \text{M} \rightarrow \text{NaCl} + \text{M}$	$1 \times 10^{-28} \text{T}^{-1}$	30	100
F7	$\text{K} + \text{Cl} + \text{M} \rightarrow \text{KCl} + \text{M}$	$1 \times 10^{-28} \text{T}^{-1}$	30	100
F8	$\text{Cs} + \text{Cl} + \text{M} \rightarrow \text{CsCl} + \text{M}$	$1 \times 10^{-28} \text{T}^{-1}$	30	100
G1	$\text{Li}^+ + \text{e}^- + \text{M} \rightarrow \text{Li} + \text{M}$	$2 \times 10^{-20} \text{T}^{-2}$	3	3
G2	$\text{Na}^+ + \text{e}^- + \text{M} \rightarrow \text{Na} + \text{M}$	$1.5 \times 10^{-20} \text{T}^{-2}$	3	3
G3	$\text{K}^+ + \text{e}^- + \text{M} \rightarrow \text{K} + \text{M}$	$2 \times 10^{-22} \text{T}^{-1.5}$	3	3
G4	$\text{Cs}^+ + \text{e}^- + \text{M} \rightarrow \text{Cs} + \text{M}$	$2 \times 10^{-22} \text{T}^{-1.5}$	5	5
H1	$\text{Li}^+ + \text{Cl}^- \rightarrow \text{Li} + \text{Cl}$	$2 \times 10^{-7} \text{T}^{-0.5}$	10	100
H2	$\text{Na}^+ + \text{Cl}^- \rightarrow \text{Na} + \text{Cl}$	$2 \times 10^{-7} \text{T}^{-0.5}$	10	10
H3	$\text{K}^+ + \text{Cl}^- \rightarrow \text{K} + \text{OH}$	$1 \times 10^{-8} \text{T}^{-0.5}$	10	100
H4	$\text{Cs}^+ + \text{Cl}^- \rightarrow \text{Cs} + \text{Cl}$	$3 \times 10^{-8} \text{T}^{-0.5}$	100	100
H5	$\text{Li}^+ + \text{OH}^- \rightarrow \text{Li} + \text{OH}$	$1 \times 10^{-7} \text{T}^{-0.5}$	10	100
H6	$\text{Na}^+ + \text{OH}^- \rightarrow \text{Na} + \text{OH}$	$1 \times 10^{-7} \text{T}^{-0.5}$	10	100
H7	$\text{K}^+ + \text{OH}^- \rightarrow \text{K} + \text{OH}$	$1 \times 10^{-7} \text{T}^{-0.5}$	10	100
H8	$\text{Cs}^+ + \text{OH}^- \rightarrow \text{Cs} + \text{OH}$	$1 \times 10^{-7} \text{T}^{-0.5}$	10	100
J1	$\text{OH} + \text{e}^- + \text{M} \rightarrow \text{OH}^- + \text{M}$	$3 \times 10^{-30}$	30	30
J2	$\text{O}_2 + \text{e}^- + \text{M} \rightarrow \text{O}_2^- + \text{M}$	$3 \times 10^{-30}$	10	10

II. LIST OF RATE CONSTANTS cont'd.

No.	Reaction		Rate Constant, k, cm-molecule-sec units	Possible Error Factor	
				Upper	Lower
J3	$\text{Cl} + \text{e}^- + \text{M} \rightarrow \text{Cl}^- + \text{M}$		$3 \times 10^{-30}$	30	30
J4	$\text{HCl} + \text{e}^- \rightarrow \text{H} + \text{Cl}^-$		$1 \times 10^{-10} e^{-20000/RT}$	300	10
J5	$\text{O} + \text{e}^- + \text{M} \rightarrow \text{O}^- + \text{M}$		$3 \times 10^{-30}$	30	30
L1	$\text{LiH}_2\text{O}^+ + \text{M} \rightarrow \text{Li}^+ + \text{H}_2\text{O} + \text{M}$		$1 \times 10^{-9} e^{-50000/RT}$	30	30
L2	$\text{NaH}_2\text{O}^+ + \text{M} \rightarrow \text{Na}^+ + \text{H}_2\text{O} + \text{M}$		$1 \times 10^{-9} e^{-35000/RT}$	30	30
L3	$\text{KH}_2\text{O}^+ + \text{M} \rightarrow \text{K}^+ + \text{H}_2\text{O} + \text{M}$		$1 \times 10^{-9} e^{-20000/RT}$	30	30
M1	$\text{LiH}_2\text{O}^+ + \text{e}^- \rightarrow \text{Li} + \text{H}_2\text{O}$		$1 \times 10^{-7}$	10	30
M2	$\text{NaH}_2\text{O}^+ + \text{e}^- \rightarrow \text{Na} + \text{H}_2\text{O}$		$1 \times 10^{-7}$	10	30
M3	$\text{KH}_2\text{O}^+ + \text{e}^- \rightarrow \text{K} + \text{H}_2\text{O}$		$1 \times 10^{-7}$	10	30
N1	$\text{LiH}_2\text{O}^+ + \text{Cl}^- \rightarrow \text{Li} + \text{Cl} + \text{H}_2\text{O}$		$1 \times 10^{-7}$	10	100
N2	$\text{NaH}_2\text{O}^+ + \text{Cl}^- \rightarrow \text{Na} + \text{Cl} + \text{H}_2\text{O}$		$1 \times 10^{-7}$	10	100
N3	$\text{KH}_2\text{O}^+ + \text{Cl}^- \rightarrow \text{K} + \text{Cl} + \text{H}_2\text{O}$		$1 \times 10^{-7}$	10	100
N4	$\text{LiH}_2\text{O}^+ + \text{OH}^- \rightarrow \text{Li} + \text{OH} + \text{H}_2\text{O}$		$1 \times 10^{-7}$	10	100
N5	$\text{NaH}_2\text{O}^+ + \text{OH}^- \rightarrow \text{Na} + \text{OH} + \text{H}_2\text{O}$		$1 \times 10^{-7}$	10	100
N6	$\text{KH}_2\text{O}^+ + \text{OH}^- \rightarrow \text{K} + \text{OH} + \text{H}_2\text{O}$		$1 \times 10^{-7}$	10	100
O1	$\text{O} + \text{Cl} + \text{M} \rightarrow \text{ClO} + \text{M}$		$2 \times 10^{-29} T^{-1}$	30	30
O2	$\text{Li} + \text{ClO} \rightarrow \text{LiCl} + \text{O}$		$2 \times 10^{-10} e^{-3000/RT}$	10	100
O3	$\text{Na} + \text{ClO} \rightarrow \text{NaCl} + \text{O}$		$2 \times 10^{-10} e^{-3000/RT}$	10	100
O4	$\text{K} + \text{ClO} \rightarrow \text{KCl} + \text{O}$		$2 \times 10^{-10} e^{-3000/RT}$	10	100
O5	$\text{H} + \text{ClO} \rightarrow \text{HCl} + \text{O}$		$3 \times 10^{-11}$	30	30
O6	$\text{O} + \text{ClO} \rightarrow \text{O}_2 + \text{Cl}$		$2 \times 10^{-11} e^{-3000/RT}$	30	30
O7	$\text{OH} + \text{ClO} \rightarrow \text{HO}_2 + \text{Cl}$		$5 \times 10^{-10}$	2	100

II. LIST OF RATE CONSTANTS cont'd

No.	Reaction		Rate Constant, k, cm-molecule-sec units	Possible Error Factor	
				Upper	Lower
P1	Li+O <sub>2</sub> +M	→ LiO <sub>2</sub> +M	1×10 <sup>-30</sup> T <sup>-1</sup>	10	10
P2	Na+O <sub>2</sub> +M	→ NaO <sub>2</sub> +M	1×10 <sup>-30</sup> T <sup>-1</sup>	10	10
P3	K+O <sub>2</sub> +M	→ KO <sub>2</sub> +M	1×10 <sup>-30</sup> T <sup>-1</sup>	10	10
P4	Cl+LiO <sub>2</sub>	→ LiCl+O <sub>2</sub>	2×10 <sup>-11</sup>	50	30
P5	Cl+NaO <sub>2</sub>	→ NaCl+O <sub>2</sub>	2×10 <sup>-11</sup>	50	30
P6	Cl+KO <sub>2</sub>	→ KCl+O <sub>2</sub>	2×10 <sup>-11</sup>	50	30
P7	H <sub>2</sub> +LiO <sub>2</sub>	→ LiOH+OH	1×10 <sup>-11</sup> e <sup>-10000/RT</sup>	50	50
P8	H <sub>2</sub> +NaO <sub>2</sub>	→ NaOH+OH	1×10 <sup>-11</sup> e <sup>-10000/RT</sup>	50	50
P9	H <sub>2</sub> +KO <sub>2</sub>	→ KOH+OH	1×10 <sup>-11</sup> e <sup>-10000/RT</sup>	50	50
P10	OH+LiO <sub>2</sub>	→ LiOH+O <sub>2</sub>	2×10 <sup>-11</sup>	50	30
P11	OH+NaO <sub>2</sub>	→ NaOH+O <sub>2</sub>	2×10 <sup>-11</sup>	50	30
P12	OH+KO <sub>2</sub>	→ KOH+O <sub>2</sub>	2×10 <sup>-11</sup>	50	30
Q1	H+O <sub>2</sub> +M	→ HO <sub>2</sub> +M	3×10 <sup>-29</sup> T <sup>-1</sup>	5	5
Q2	Cl+HO <sub>2</sub>	→ HCl+O <sub>2</sub>	2×10 <sup>-11</sup>	50	30
Q3	H+HO <sub>2</sub>	→ OH+OH	1×10 <sup>-10</sup>	10	10
Q4	H+HO <sub>2</sub>	→ H <sub>2</sub> +O <sub>2</sub>	3×10 <sup>-11</sup>	10	10
Q5	H <sub>2</sub> +HO <sub>2</sub>	→ H <sub>2</sub> O+OH	1×10 <sup>-11</sup> e <sup>-25000/RT</sup>	50	50
Q6	CO + HO <sub>2</sub>	→ CO <sub>2</sub> +OH	1×10 <sup>-11</sup> e <sup>-10000/RT</sup>	100	100
Q7	O+HO <sub>2</sub>	→ OH+O <sub>2</sub>	1×10 <sup>-11</sup>	100	10
Q8	OH+HO <sub>2</sub>	→ H <sub>2</sub> O+O <sub>2</sub>	2×10 <sup>-11</sup>	50	30
R1	CHO+O	→ CO+OH	1×10 <sup>-11</sup>	30	30
R2	CHO+OH	→ CO+H <sub>2</sub> O	1×10 <sup>-11</sup>	30	100
R3	CO+H+M	→ CHO+M	3×10 <sup>-29</sup> T <sup>-1</sup>	10	30
R4	CHO+H	→ CO+H <sub>2</sub>	1×10 <sup>-11</sup>	30	100

II. LIST OF RATE CONSTANTS cont'd.

No.	Reaction	Rate Constant, k, cm-molecule-sec units	Possible Error Factor	
			Upper	Lower
S1	$\text{Cl} + \text{OH} + \text{M} \rightarrow \text{ClOH} + \text{M}$	$3 \times 10^{-29} \text{T}^{-1}$	30	30
S2	$\text{ClOH} + \text{H} \rightarrow \text{ClO} + \text{H}_2$	$1 \times 10^{-11}$	100	100
S3	$\text{ClOH} + \text{OH} \rightarrow \text{ClO} + \text{H}_2\text{O}$	$1 \times 10^{-11}$	100	100
S4	$\text{ClOH} + \text{O} \rightarrow \text{ClO} + \text{OH}$	$2 \times 10^{-11}$	100	100
T1	$\text{CH}_4 + \text{OH} \xrightarrow{\text{---}} \text{CO} + \text{H}_2\text{O}$	$5 \times 10^{-11} e^{-5000/\text{RT}}$	5	5
T2	$\text{CH}_4 + \text{OH} \xrightarrow{\text{---}} \text{H}_3\text{O}^+ + \text{e}^- + \text{CO}_2$	$5 \times 10^{-17} e^{-5000/\text{RT}}$	10	10
T3	$\text{CH} + \text{O} \rightarrow \text{CHO}^+ + \text{e}^-$	$5 \times 10^{-12}$	10	10
T4	$\text{CHO}^+ + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{CO}$	$1 \times 10^{-8}$	5	5
T5	$\text{H}_3\text{O}^+ + \text{Li} \rightarrow \text{Li}^+ + \text{H}_2\text{O} + \text{H}$	$1 \times 10^{-8}$	5	5
T6	$\text{H}_3\text{O}^+ + \text{Na} \rightarrow \text{Na}^+ + \text{H}_2\text{O} + \text{H}$	$1 \times 10^{-8}$	5	5
T7	$\text{H}_3\text{O}^+ + \text{K} \rightarrow \text{K}^+ + \text{H}_2\text{O} + \text{H}$	$1 \times 10^{-8}$	5	5
T8	$\text{H}_3\text{O}^+ + \text{Cs} \rightarrow \text{Cs}^+ + \text{H}_2\text{O} + \text{H}$	$1 \times 10^{-8}$	5	5
T9	$\text{H}_3\text{O}^+ + \text{e}^- \rightarrow \text{H} + \text{H} + \text{OH}$	$2 \times 10^{-7}$	1.5	1.5
T10	$\text{H}_3\text{O}^+ + \text{Cl}^- \rightarrow \text{H} + \text{OH} + \text{HCl}$	$3 \times 10^{-8}$	10	10
T11	$\text{H}_3\text{O}^+ + \text{OH}^- \rightarrow \text{H} + \text{OH} + \text{H}_2\text{O}$	$8 \times 10^{-8}$	10	10

III. NOTES ON RATE CONSTANTS

- A1 Frisvrom and Westenberg<sup>7</sup> recommend the work of Morgan and Schiff<sup>3</sup> as the only unambiguous work on direct recombination. For  $M \equiv N_2$ , these authors give  $k_{A1} = 3 \times 10^{-33}$  at room temperature, which might suggest  $k_{A1} = 10^{-30} T^{-1}$ . Shock tube studies<sup>4-7</sup> on the reverse reaction would imply that  $k_{A1}$  should be much larger, and suggest that the  $T^{-1}$  temperature dependence is reasonable in the range  $1500 < T < 3500$ . Note that dissociation rate constants given in Refs. 5, 6, and 7 agree quite well with each other and have pre-exponential factors some 100 times larger than the collision frequency. The recombination rate constant given<sup>3</sup> implies a pre-exponential factor in the rate constant for the dissociation reaction of only 10 times the collision frequency. Discrepancies could perhaps be explained in terms of deviations from the macroscopic rate quotient law. The value of  $k_{A1}$  given seems a reasonable compromise for an "average" third-body M.
- A2 It appears that no experimental work has been done on this reaction. The rate constant given is estimated by comparison with rate constants for other reactions in Group A.
- A3 Work reported in Ref. 2 suggests, for various third bodies,
- $$\begin{aligned}
 k_{A3} &= 3 \times 10^{-29} T^{-1} & (M \equiv H) \\
 k_{A3} &= 1 \times 10^{-29} T^{-1} & (M \equiv H_2) \\
 k_{A3} &= 4 \times 10^{-30} T^{-1} & (M \equiv \text{rare gas atom}) \\
 k_{A3} &\sim 4 \times 10^{-29} T^{-1} & (M \equiv H_2O)
 \end{aligned}$$
- The direct measurements available<sup>2</sup>, however, are in considerable disagreement, and shock tube measurements on the reverse reaction are also difficult to interpret<sup>2</sup>. The value given is in reasonable agreement with Refs. 8 and 9, which describe the most convincing experiments. It implies a pre-exponential factor in the rate constant for the reverse reaction of several hundred times the collision frequency. Our practice of listing rate constants for "average" third bodies is open to considerable doubt in this case;  $H_2O$  appears to be very much more efficient than  $H_2$ , for example.
- A4 Little reliable data is available for this reaction. The agreement between independent values of  $k_{A4}$  obtained by Bulewicz and Sugden<sup>10</sup> and by McAndrew and Wheeler<sup>11</sup>, for example, is fortuitous in view of the lack of distinction between contributions from

III. NOTES ON RATE CONSTANTS cont'd.

and



in the former work. Schott and Bird<sup>9</sup> appear to have obtained a reasonably reliable value, however, and the wide error limits suggested above reflect uncertainties in third-body efficiencies. The rate constant given corresponds to a very large ( $\sim 3 \times 10^{-7}$ ) pre-exponential factor in the reverse reaction.

A5 The surprising exponential term is suggested by the work of Clyne and Thrush<sup>12</sup> at temperatures lower than those encountered in rocket exhausts. At 2000<sup>o</sup>K, the exponential term does not carry a great deal of weight by comparison with the uncertainties in the rate constant as a whole. Zeegers' work<sup>13</sup> suggests that O<sub>2</sub> has a very high third-body efficiency in this reaction ( $k_{A5} \sim 1.2 \times 10^{-31}$  for M  $\equiv$  O<sub>2</sub> at 2350<sup>o</sup>K) but that CO<sub>2</sub> is inefficient ( $k_{A5} \sim 2.4 \times 10^{-33}$  for M  $\equiv$  CO<sub>2</sub> at 2350<sup>o</sup>K). The value of  $k_{A5}$  listed is probably an upper-limit value.

A6 This value is taken from the work of Kaufman and del Greco<sup>14</sup>. Work on the reaction is reviewed by these authors.

B1 Fristrom and Westenberg<sup>2</sup> recommend a rate constant for the reverse of Reaction B1 of  $8.3 \times 10^{-11} e^{-20,000/RT}$ , and an equilibrium constant of  $0.21 e^{15175/RT}$ . These figures correspond to  $k_{B1} = 1.75 \times 10^{-11} e^{-4800/RT}$ . Dixon-Lewis, Sutton, and Williams<sup>15</sup> suggest that the reverse reaction rate constant is  $1.5 \times 10^{-10} e^{-20400/RT}$ , and hence  $k_{B1} = 3 \times 10^{-11} e^{-5000/RT}$ . However, the results at higher temperatures (see Ref. 2) do suggest a somewhat higher activation energy for each reaction. The rate constant given above agrees with that obtained by the various workers at about 900<sup>o</sup>K, but is slightly preferable for the temperature range (1000 to 3500<sup>o</sup>K) of interest. It is also in good agreement with the value given recently<sup>16</sup> by Dixon-Lewis, Wilson, and Westenberg.

B2 Fristrom and Westenberg<sup>2</sup> suggest  $k_{B2} = 2 \times 10^{-11} e^{-9400/RT}$ , but their estimate is perhaps rather too heavily weighted in favor of the results of Clyne and Thrush<sup>17</sup>, and the results in Fig. XIV-20 of Ref. 2 themselves suggest a somewhat lower activation energy. The rate constant given above is in fair agreement with the results of Wong and Potter<sup>18</sup> and of Kurzius<sup>19</sup> and seems a fair compromise.

III. NOTES ON RATE CONSTANTS cont'd

- B3 This reaction has been studied over a very wide range of temperatures<sup>2</sup>. Fristrom and Westenberg<sup>2</sup> recommend a rate constant of  $3.7 \times 10^{-10} e^{-16500/RT}$ . Kurzius<sup>19</sup> finds  $k_{B3} = 2.3 \times 10^{-10} e^{-16200/RT}$ . It is difficult to see how this rate constant can be greatly in error in the temperature range of interest.
- B4 Analysis of earlier results by Fristrom and Westenberg<sup>2</sup> led these authors to suggest a rate constant of about  $1 \times 10^{-11} e^{-7700/RT}$  for this reaction. More recent results<sup>16, 20</sup>, however, suggest that such an activation energy would be far too high; we have adopted the value given by Dixon-Lewis, Wilson, and Westenberg<sup>16</sup> as the best available at present.
- C1 The rate constant given was estimated by Fristrom and Westenberg<sup>2</sup> on the basis of results obtained by Klein and Wolfsberg<sup>21</sup>.
- C2 The estimates of this rate constant given by Fristrom and Westenberg<sup>2</sup> and by Fettis and Knox<sup>22</sup> are in good agreement with one another. The rate constant given above is based on these two estimates.
- C3 This rate constant is estimated by comparison with that for the reverse of C1, due allowance being made for a steric hindrance factor and for an activation energy 4000 cal/mole greater than the endothermicity.
- C4 The rate constant given is estimated by comparison with that for  $OH + H \rightarrow H_2 + O$  ( $k = 1.3 \times 10^{-11} e^{-6300/RT}$ ). Each of these reactions is spin allowed and approximately thermoneutral.
- C5 This rate constant is the result of an experimental study of the kinetics of decomposition of HF by Jacobs, Giedt, and Cohen<sup>31</sup>. Note that the pre-exponential factor in the rate constant for the similar reaction  $H + HCl \rightarrow H_2 + Cl$  (reverse of C2) is<sup>2</sup>  $1.0 \times 10^{-10}$ , which is somewhat higher than that in  $k_{C5}$ .
- C6 This rate constant is estimated by comparison with  $k_{C1}$ . The pre-exponential factor is approximately equal to the collision frequency. The reaction, like C1, is strongly exothermal.

III. NOTES ON RATE CONSTANTS cont'd

D1 This rate constant is estimated by comparison with those of D2 and D3, the bond energy of LiCl being known.<sup>23</sup>

D2 This estimate is based on measurements made by Polanyi<sup>24</sup> in 1932; no recent measurements appear to be available. However, Kondratiev<sup>25</sup> reports results of Taylor and Datz<sup>26</sup> which suggest that the rate constant of the reaction



is given by

$$k = 3.0 \times 10^{-12} T^{0.5} e^{-3400/RT},$$

or, at 1600°K, by

$$k = 1.2 \times 10^{-10} e^{-3400/RT}.$$

In the experiments of Taylor and Datz,  $500 < T < 3000^\circ\text{K}$ . These results and others<sup>25</sup> suggest that the pre-exponential factors of rate constants of reactions like D2 are close to the collision frequencies, and the rate constant for D2 given above stems from adoption of this suggestion. Taylor and Datz used a molecular beam technique; the early work suffers from uncertainties concerning the possible effects of solid particles.<sup>24</sup>

D3 This rate constant also is based on the work of Polanyi<sup>24</sup> and the discussion given by Kondratiev.<sup>25</sup>

D4 The rate constant recommended is based on a comparison of D4 with D2 and D3, the bond energy of CsCl<sup>23</sup> being borne in mind.

D5 This rate constant was estimated on the basis of arguments given by Sugden<sup>27</sup> and experimental evidence obtained by Jensen<sup>28</sup> and Jensen and Padley.<sup>29</sup> The activation energy is estimated through reference to the work of Jensen and Padley;<sup>30</sup> 3000 cal/mole are arbitrarily added to the known<sup>30</sup> endothermicity.



III. NOTES ON RATE CONSTANTS cont'dD6, D7, D8

Estimated in a manner similar to that in which  $k_{D5}$  was obtained.

- E1 No experimental data appear to be available for this reaction. The value given for  $k_{E1}$  is estimated through comparison with rate constants for other ternary reactions, including E3.
- E2 The work of Jacobs and Giedt<sup>32</sup> suggests a rate constant smaller by a factor of 10 than that given in Section II. Hiraoka and Hardwick<sup>33</sup>, on the other hand, find that  $k_{E2} = 7 \times 10^{-33}$  at 1600°K for argon as a third body. This would correspond to our value for molecular third bodies, assumed to be 3 times as efficient as Ar. Fristrom and Westenberg<sup>2</sup> suggest why the results of Hiraoka and Hardwick are to be preferred to those of Jacobs and Giedt.
- E3 This rate constant has been measured<sup>31</sup> with Ar as third body in the temperature range 4000<T<5300°K. The results obtained could be described in terms of  $k_{E3,Ar} = 5 \times 10^{-29}T^{-1}$ , but the scatter of results was rather large. Multiplication of  $k_{E3,Ar}$  by 5 to allow for greater efficiency of molecular third bodies would give  $k_{E3} = 2.5 \times 10^{-28}T^{-1}$ . This seems rather high, however, and the value given in Section II is preferred as a compromise until further work is done. Note that the experimental rate constant found by Jacobs, Giedt and Cohen<sup>31</sup> is of the same order of magnitude as that predicted by Benson and Fueno<sup>65</sup>.
- E4 The rate constant for this reaction is based on the work of Johnson and Britton<sup>63</sup> and Diesen<sup>64</sup>, who studied the dissociation of F<sub>2</sub> by Ar in shock tubes. The temperature-dependence given corresponds approximately to that found for the reverse of reaction E4 by Johnson and Britton; that suggested by Diesen's work appears improbably high. Allowance is made for molecules in rocket exhausts being more efficient in producing dissociation than Ar atoms. Note that the pre-exponential factor in the rate constant for the reverse of Reaction E4 is considerably smaller than those of corresponding rate constants for the other halogens.<sup>64</sup>
- F1 This is a very high rate constant, although certainly not the highest ever suggested for a ternary recombination reaction--see, for example, Ref. 11. Combination of theoretical arguments of Sugden<sup>27</sup>

III. NOTES ON RATE CONSTANTS cont'd.

and experimental results of Jensen and Padley<sup>29, 30</sup> and Bulewicz and Sugden<sup>34</sup> shows that the rate constant for the reverse of Reaction F1 cannot be much smaller than  $6 \times 10^{-4} T^{-1} e^{-101000/RT}$ , and that  $k_{F1}$  therefore cannot be much smaller than  $10^{-27} T^{-1}$ . (The equilibrium constant for reaction F1 is approximately  $1.6 \times 10^{-24} e^{101000/RT}$ .) The value of  $k_{F1}$  recommended above seems a reasonable compromise: it is not much smaller than  $10^{-27} T^{-1}$  and not much greater than the rather high rate constant for the formally similar Reaction A4.

F2, F3, F4

Estimated in a manner similar to that in which  $k_{F1}$  was obtained.

F5 No experimental data are available for this reaction. The rate constant  $k_{F5}$  is perhaps likely to be somewhat smaller than that for Reaction F1 (the collision is less "sticky"--note that  $k_{E1} < k_{A4}$ ). The value given above is (for no particularly good reason) the geometric mean of  $k_{E2}$  and  $k_{F1}$ . The error limits quoted are consequently very large.

F6, F7, F8

Estimated in a manner similar to that in which  $k_{F5}$  was obtained.

G1 This rate constant was calculated from measurements on the reverse reaction by Jensen and Padley<sup>29, 35</sup> at 2475°K. The temperature dependence is assumed to be the same as that of  $k_{G2}$ . All molecular third bodies are assumed to have equal third-body efficiencies in G1<sup>29, 35</sup>; atomic third bodies are less efficient.<sup>36</sup>

G2 Jensen and Padley<sup>29, 35</sup> measured the rate constant of the reverse reaction at 2020 to 2450°K at atmospheric pressure in  $H_2/N_2/O_2$  flames and calculated  $k_{G2} = 1.4 \times 10^{-20} T^{-2}$ . Hollander, Alkemade, and Kalff<sup>37</sup>, using  $CO/N_2/O_2$  flames in a similar (but narrower) range of temperature, find  $k = 1.6 \times 10^{-20} T^{-2}$ . Molecular third bodies tend to have approximately equal efficiencies in this reaction, but atomic third bodies are much less efficient<sup>36</sup>.

G3 This rate constant was calculated from measurements on the reverse reaction by Jensen and Padley<sup>29, 35</sup>. The corresponding value for atmospheric-pressure  $CO/N_2/O_2$  flames is  $1.5 \times 10^{-22} T^{-1.5}$ .

III. NOTES ON RATE CONSTANTS cont'd.

G4 This rate constant was calculated from measurements on the reverse reaction by Jensen and Padley<sup>29, 35</sup>. Hollander, Alkemade and Kalff<sup>37</sup> find a much smaller rate constant ( $2 \times 10^{-23} T^{-1.5}$ ) in CO/N<sub>2</sub>/O<sub>2</sub> flames. Jensen and Padley's results are preferred (a) because two independent analytical techniques (optical emission spectroscopy and microwave cavity resonance) gave the same rate constant--within the limits of experimental error--in their work, and (b) because the order of magnitude of their results is consistent with equilibrium ionization of cesium being closely approached under conditions employed by other workers<sup>37-40</sup>, whereas that of Hollander, Alkemade, and Kalff's results is not.

H1 This rate constant is estimated by comparison with  $k_{H2}$  and  $k_{H3}$ . It may be noted that the above value of  $k_{H1}$  corresponds to a rate constant for the reverse reaction of  $4 \times 10^{11-10} e^{-34000/RT}$  at 2000°K: the pre-exponential factor of the reverse reaction rate constant is thus close to the collision frequency. It should also be borne in mind that uncertainties in crossings of potential energy curves cause one to doubt the validity of our simplified approach to the determination of Group H rate constants. We have implicitly assumed, for example, that for Reaction H1 the potential energy curves involved are favorably placed with respect to one another.

H2 An approximate value for this rate constant was measured by Hayhurst<sup>39</sup> and is discussed by Hayhurst and Sugden<sup>41, 42</sup>. Note that Baulknight and Bortner<sup>43</sup> estimate the following theoretical rate constants:



Comparison with these estimates led us to insert a  $T^{-0.5}$  temperature dependence in  $k_{H2}$ ; Sugden<sup>44</sup> reports that the measured temperature dependence is slight.

H3 This rate constant was measured by Hayhurst<sup>39</sup> and reported by Sugden and Hayhurst<sup>41</sup>. For the origin of the temperature dependence of  $k_{H3}$ , see the note to Reaction H2.

H4 This rate constant is estimated by comparison with rate constants for Reactions H2 and H3. See also the note to Reaction H1.

III. NOTES ON RATE CONSTANTS cont'd

H5 This rate constant is estimated by comparison with  $k_{H1}$  and the rate constants<sup>43</sup> suggested for the reactions



Our estimate implies that the pre-exponential factor of the reverse reaction rate constant is close to the collision frequency.

H6, H7, H8

Estimated in a manner similar to that in which  $k_{H5}$  was obtained.

J1 This rate constant is taken to be the same as that for Reaction J2. It is difficult to justify this assumption, but equally difficult to suggest a better means of estimating  $k_{J1}$  on the basis of present knowledge.

J2 The value of  $k_{J2}$  given is based on measurements made at about 500°K by Pack and Phelps<sup>45,46</sup>. These authors found that  $k_{J2}$  increased slightly with increasing temperature, which is perhaps contrary to what one might expect. We have used a temperature-independent value for 1000 < T < 3500°K. The data on third-body relative efficiencies are meager; Pack and Phelps find that H<sub>2</sub>O is about four times as efficient as O<sub>2</sub> in Reaction J2. For a review of attachment of electrons to O<sub>2</sub>, see Ref. 47.

J3 This rate constant is taken to be the same as that for Reaction J2.

J4 This rate constant was estimated by Calcote and Jensen<sup>48</sup> on the basis of collision cross-section data obtained by Buchel'nikova<sup>49</sup>. Note, however, that recent results of Fehsenfeld, Ferguson, and Schmeltekopf suggest that the reaction may be considerably faster<sup>50</sup>.

J5 Estimated in a manner similar to that in which  $k_{J3}$  was obtained.

L1 This rate constant was estimated by Calcote and Jensen<sup>48</sup> on the basis of results obtained by Hayhurst<sup>39,51</sup> and Hayhurst and Sugden<sup>42</sup>,

L2, L3

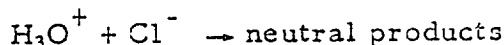
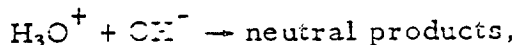
Estimated in a manner similar to that in which  $k_{L1}$  was obtained.

M1 This rate constant is estimated by comparison with the known rate constant of Reaction T9.

III. NOTES ON RATE CONSTANTS cont'd.M2, M3

Estimated in a manner similar to that in which  $k_{M1}$  was obtained.

N1 Estimated by comparison with preliminary values for the rate constants of the reactions



measured by Calcote and Kurzius<sup>53</sup>.

N2, N3, N4, N5, N6

Estimated in a manner similar to that in which  $k_{N1}$  was obtained.

O1 This rate constant is estimated by comparison with the values of  $k_{A1}$  and  $k_{E2}$ .

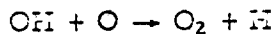
O2 The pre-exponential factor in  $k_{O2}$  is thought likely to be close to the collision frequency. An arbitrary activation energy of 3000 cal/mole has been inserted (the reaction is 52 kcal/mole exothermic) as a result of comparison with other bimolecular reactions.

O3, O4

Estimated in a manner similar to that in which  $k_{O2}$  was obtained.

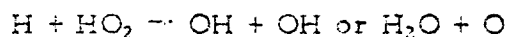
O5 This rate constant is estimated by comparison with  $k_{B2}$  and  $k_{C4}$ .

O6 This reaction is thought by Kaufman<sup>54</sup> to be rapid at room temperature, which would imply that the activation energy is small. We have arbitrarily set the activation energy equal to 3000 cal/mole. Comparison of this reaction with

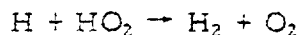


would suggest a pre-exponential factor of about  $2 \times 10^{-11}$ .

O7 The rate constant for the reverse reaction of O7 is estimated by comparison with the rate constant of Q3; both these reactions proceed with essentially zero activation energy. Note that the ratio of the rate constant of the reverse of Reaction O7 to  $k_{Q2}$  has been set equal to 3:1, which is also the ratio of the rate constants of

III. NOTES ON RATE CONSTANTS cont'd.

and

according to Clyne and Thrush<sup>55</sup>.P1 Estimated by comparison with  $k_{P2}$ .P2 This rate constant is estimated from the work of Carabetta and Kaskan<sup>56</sup>, who found values of  $k_{P2}$  ranging from  $6.0 \times 10^{-34}$  to  $8.2 \times 10^{-34}$  over the temperature range  $1540 < T < 1730$ . This work was done on clean  $\text{H}_2/\text{CO}/\text{air}$  flames at 100 Torr.P3 Estimated by comparison with  $k_{P2}$ .P4, P5, P6Estimated by comparison with  $k_{Q4}$ .P7, P8, P9Estimated by comparison with  $k_{Q5}$ .P10, P11Estimated in a manner similar to that in which  $k_{Q8}$  was obtained.Q1 This reaction has been quite widely studied. Getzinger and Schott<sup>57</sup> found  $k_{Q1} = 3.9 \times 10^{-33}$  for  $\text{M} \equiv \text{Ar}$  at  $1500^\circ\text{K}$  in a shock tube. Clyne and Thrush<sup>55</sup>, using a fast flow discharge system, found  $k_{Q1} = 35 \times 10^{-33}$  at  $225^\circ\text{K}$ ,  $k = 40 \times 10^{-33}$  at  $244^\circ\text{K}$  and  $k_{Q1} = 22 \times 10^{-33}$  at  $293^\circ\text{K}$  for  $\text{M} \equiv \text{Ar}$ . Baldwin<sup>58</sup> gives values obtained from second explosion limit studies; for  $\text{Ar} \equiv \text{M}$ ,  $k_{Q1} = 4.7 \times 10^{-33}$  at  $813^\circ\text{K}$ , and for  $\text{H}_2 \equiv \text{M}$ ,  $k_{Q1} = 23 \times 10^{-33}$  at  $813^\circ\text{K}$ . Kurzius<sup>19</sup> found  $k_{Q1} = 30 \times 10^{-33}$  at  $800^\circ\text{K}$  for  $\text{M} \equiv \text{H}_2$  in his first explosion limit studies. The value given in Section II for a "general" third body thus seems fairly reliable.Q2 This rate constant is estimated by comparison with  $k_{Q4}$ .

III. NOTES ON RATE CONSTANTS cont'd.

Q3 This rate constant was estimated by Dixon-Lewis and Williams<sup>59</sup> to be  $1.1 \times 10^{-10}$  at  $500^\circ\text{K}$ , on the basis of data from several sources. One might note that the species H and  $\text{HO}_2$  are thought to produce  $\text{H}_2\text{O}$  and O at a small proportion of collisions.

Q4 This rate constant is estimated by comparison with  $k_{\text{Q3}}$ ; Clyne and Thrush<sup>55</sup> obtained a value of  $3 \pm 1$  for the ratio of the rate of chain propagation to the rate of chain breaking in the reaction between H and  $\text{HO}_2$ .

Q5 The rate constant of the reaction between  $\text{H}_2$  and  $\text{HO}_2$  was estimated by Dixon-Lewis and Williams<sup>59</sup> to be  $2.2 \times 10^{-18}$  at  $500^\circ\text{K}$ . These authors made use of data from several sources. This estimate is some 50 times greater than that made earlier by Voevodsky and Tal'rose,<sup>60</sup> who suggested  $k_{\text{Q5}} = 2 \times 10^{-13} e^{-24000/\text{RT}}$ . It is important to note that the reaction is thought<sup>59</sup> to lead to  $\text{H}_2\text{O}_2 + \text{H}$  rather than to  $\text{H}_2\text{O} + \text{OH}$ , as written above. We have elected to eliminate  $\text{H}_2\text{O}_2$  from our programs as a result of its relative unimportance as a reaction intermediate in high-temperature environments. The overall reaction Q5, as we write it, is satisfactory for the purposes of our programs.

Q6 This rate constant is estimated by comparison with  $k_{\text{B4}}$  and  $k_{\text{Q5}}$ . Reaction Q6 is thought by Baldwin and others<sup>61</sup> to be important at temperatures as low as  $500^\circ\text{C}$ , which in itself argues against an activation energy much higher than 10,000 cal/mole.

Q7, Q8

Estimated by comparison with  $k_{\text{Q4}}$ .

R1 Estimated in a manner similar to that in which  $k_{\text{R2}}$  was obtained.

R2 No quantitative data are available for this reaction. The rate constant given is estimated by comparison with  $k_{\text{B4}}$ ,  $k_{\text{Q3}}$ , and the rate constant for the reaction



given by Avramenko and Lorentso<sup>62</sup>.

R3 No quantitative data are available for this reaction. The rate constant given is estimated by comparison with  $k_{\text{A4}}$  and  $k_{\text{A5}}$ .

### III. NOTES ON RATE CONSTANTS cont'd.

R4 Estimated in a manner similar to that in which  $k_{R2}$  was obtained.

S1 Estimated by comparison with  $k_{O1}$ .

S2, S3, S4

Estimated in a manner similar to that in which  $k_{R2}$  was obtained.

T1 This "rate constant" is based upon the recommendation of Wilson and Westenberg<sup>66</sup> for the rate constant of the reaction between  $CH_4$  and OH and on the arguments presented by Calcote and Pergament<sup>1</sup> for use of an artificial overall reaction for oxidation of methane.

T2 The artificial overall "rate constant" was estimated by Calcote and Pergament<sup>1</sup>.

T3 The value given for  $k_{T3}$  is a compromise between theoretical values of  $3 \times 10^{-12}$  and  $1 \times 10^{-11}$  reported by Green and Sugden<sup>67</sup> and by Calcote<sup>68</sup>, respectively.

T4 This rate constant is based on arguments put forward by Calcote<sup>68</sup>.

T5 This rate constant is estimated by comparison with  $k_{T6}$ .

T6 Hayhurst and Telford<sup>69</sup> measured this rate constant in the range  $1800 < T < 2500^\circ K$ . They observed little significant dependence of  $k_{T6}$  on temperature.

T7, T8

These rate constants are estimated by comparison with  $k_{T6}$ .

T9 This rate constant has been measured by several workers; the most up-to-date value is given by Calcote, Kurzius and Miller<sup>52</sup>.

T10, T11

These preliminary values for  $k_{T10}$  and  $k_{T11}$  were measured by Calcote and Kurzius<sup>53</sup>.



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